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Structure-effect relationship between modern superplasticizers and the rheological properties of fresh cement pastes

Raphael Breiner, <u>Michael Haist</u> and Harald S. Müller
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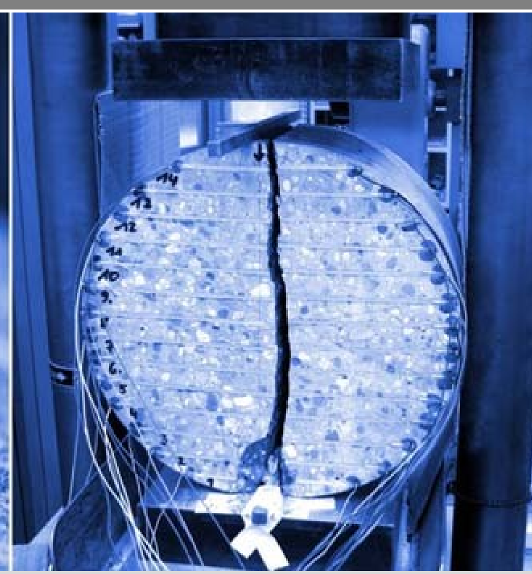
IMB KARLSRUHE



25. Kolloquium
Rheologische Messungen an mineralischen Baustoffen

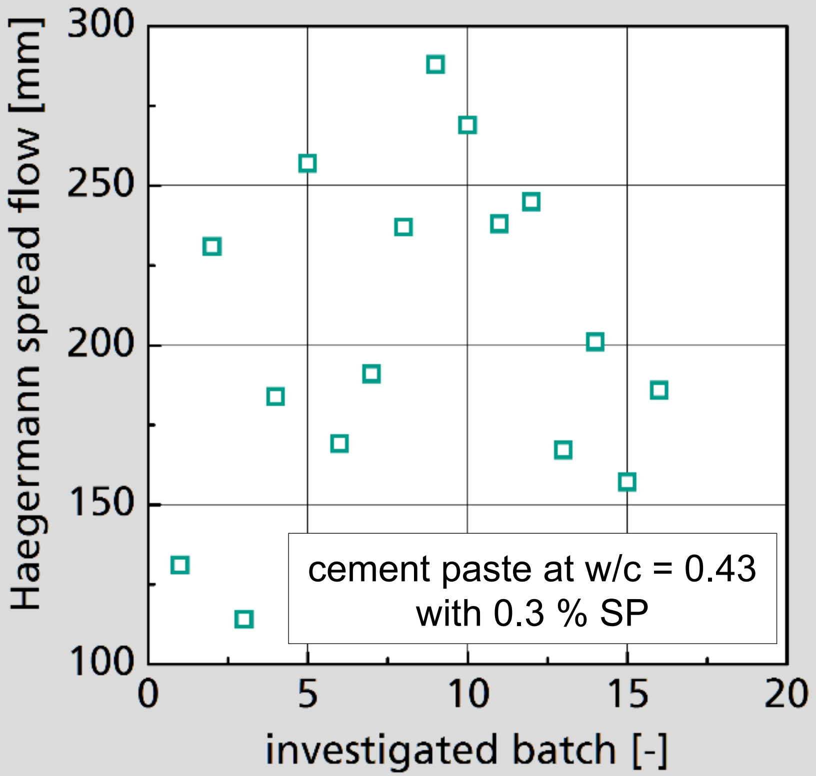
2.+3. März 2016
OTH Regensburg

Motivation

Typical problems observed in practice

- incompatibilities between cement and superplasticizers (SP) lead to insufficient rheological properties
- no systematic correlation between SP-structure, cement properties and rheological behaviour of paste known
- empiricism in the mix design process ("Trial and Error")
- damages on concrete structures may occur

Scattering properties due to cement-superplasticizer incompatabilities

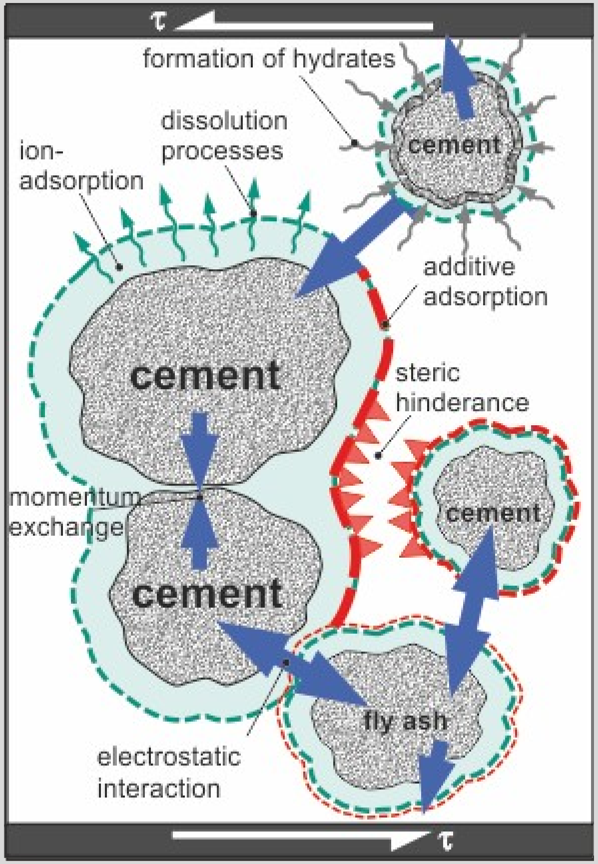


Goal of the project

Modelling of effect of SP dosage on rheology

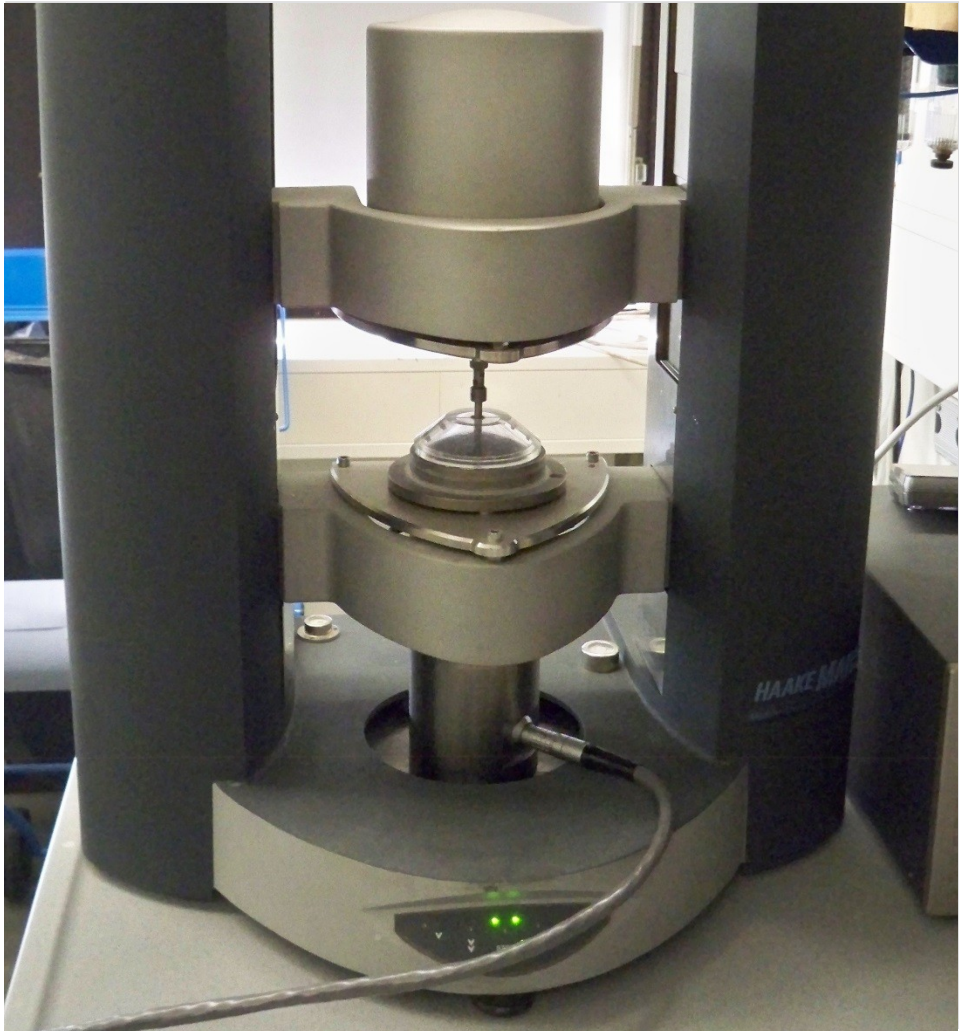
1. Understanding the particle-particle and particle-fluid interaction with and without the presence of superplasticizers
2. Quantification of the influence of superplasticizers on the rheological properties of fresh cement pastes
3. Modelling the rheological properties of fresh cement suspensions with and w/o SP as a function of the physical properties of the raw materials

Rheology of cement paste



Flow behaviour of pure cement pastes

Measurement set-up



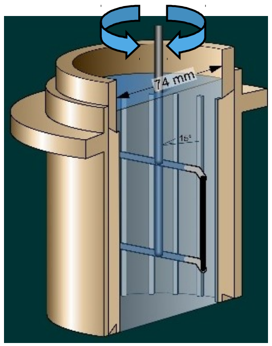
Combined measurement of

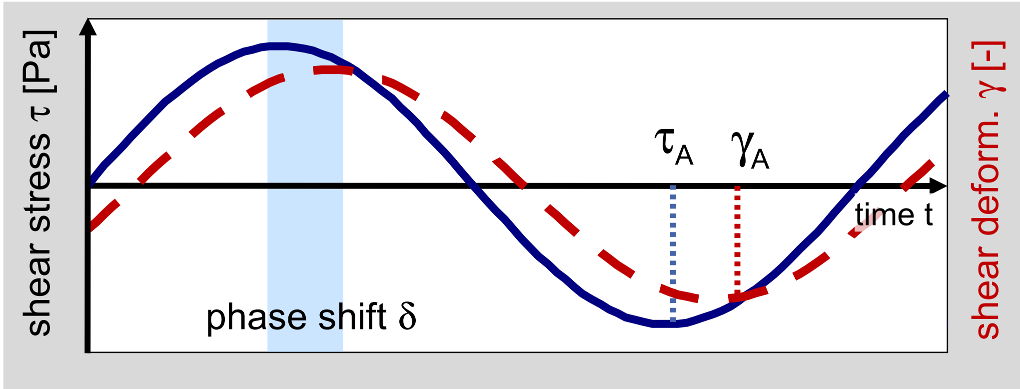
rheological properties

inter-
action

zeta-potential
and degree of agglomeration
of particles

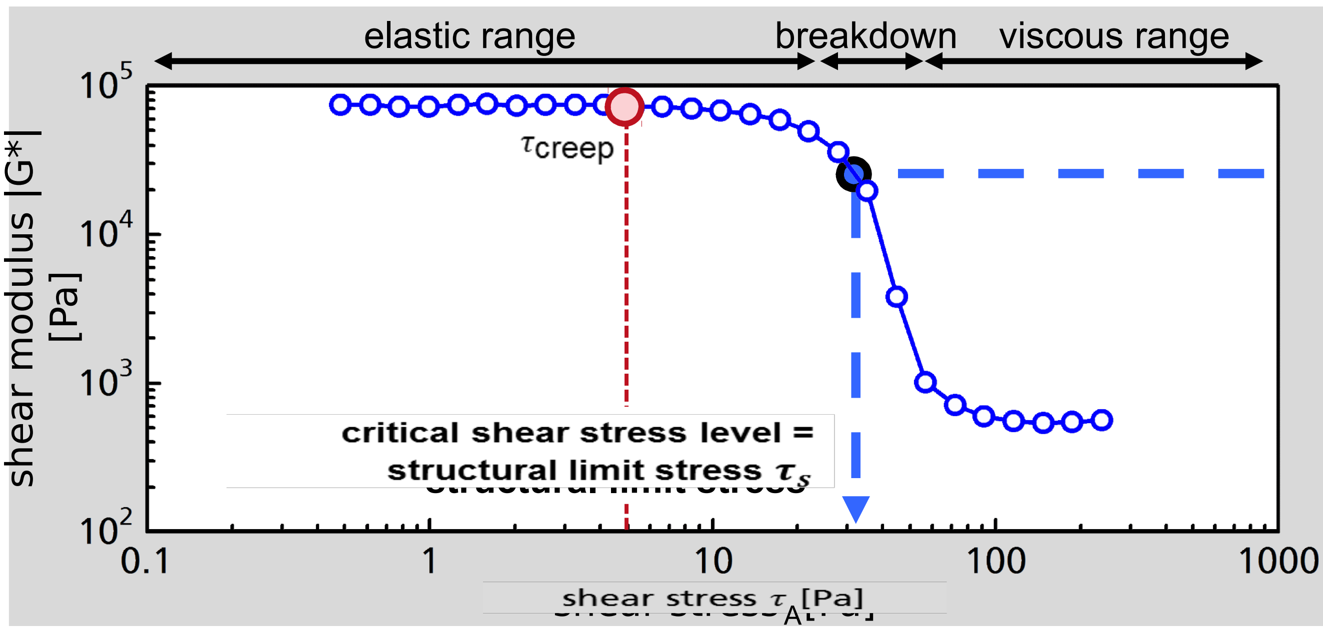
Elastic properties of fresh cement pastes





Characteristics

- shear modulus
  $G^* = \tau_A / \gamma_A$
- viscoelasticity
  phase shift δ



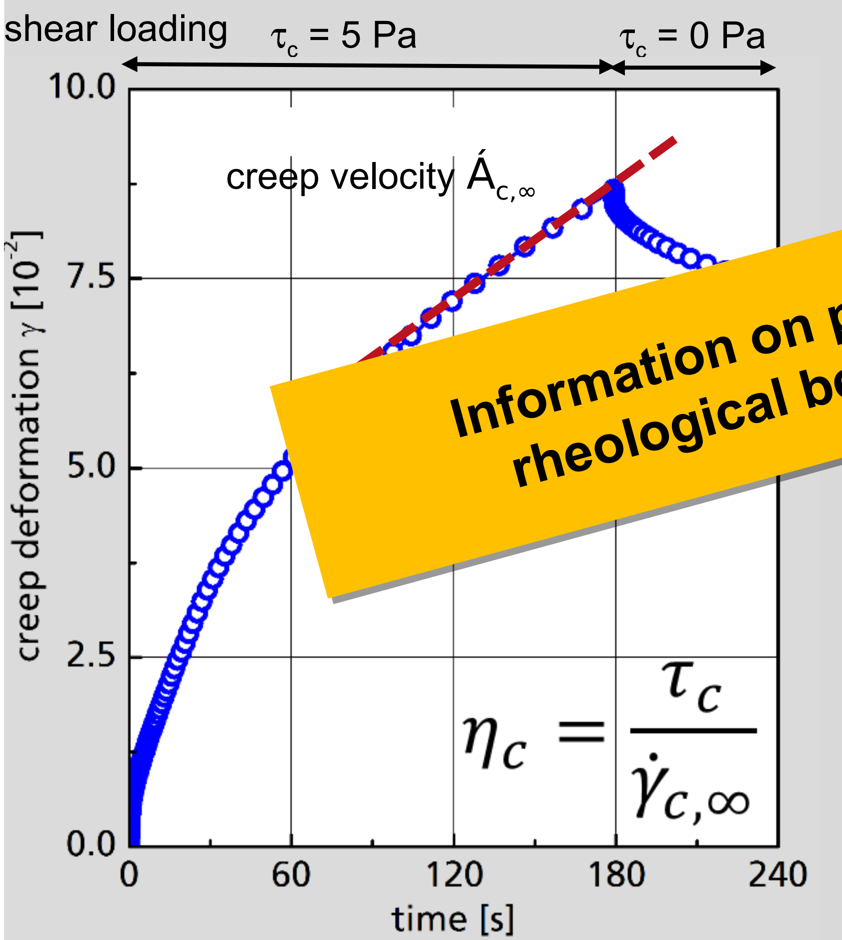
Conclusions

shear deformation characterized by:

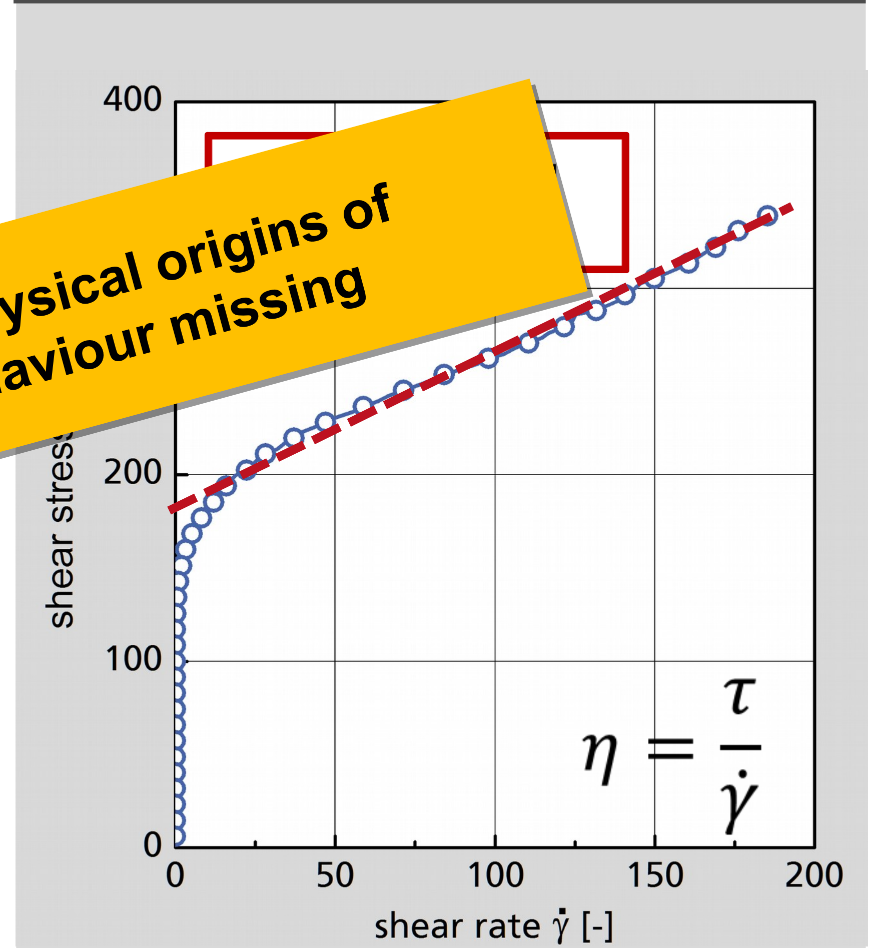
- elastic material response with const. shear modulus for low shear stresses
- strutural breakdown when critical stress level is exceeded

Creep deformation at subcritical shear stresses

Viscous flow at low shear loadings



Viscous flow at high shear loadings



Information on physical origins of rheological behaviour missing

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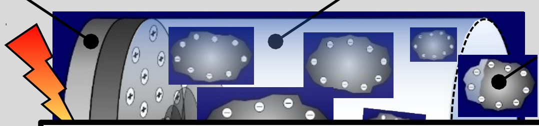
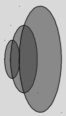
Measurement of particle interactions

Measurement principle



elektrod



ultras

p

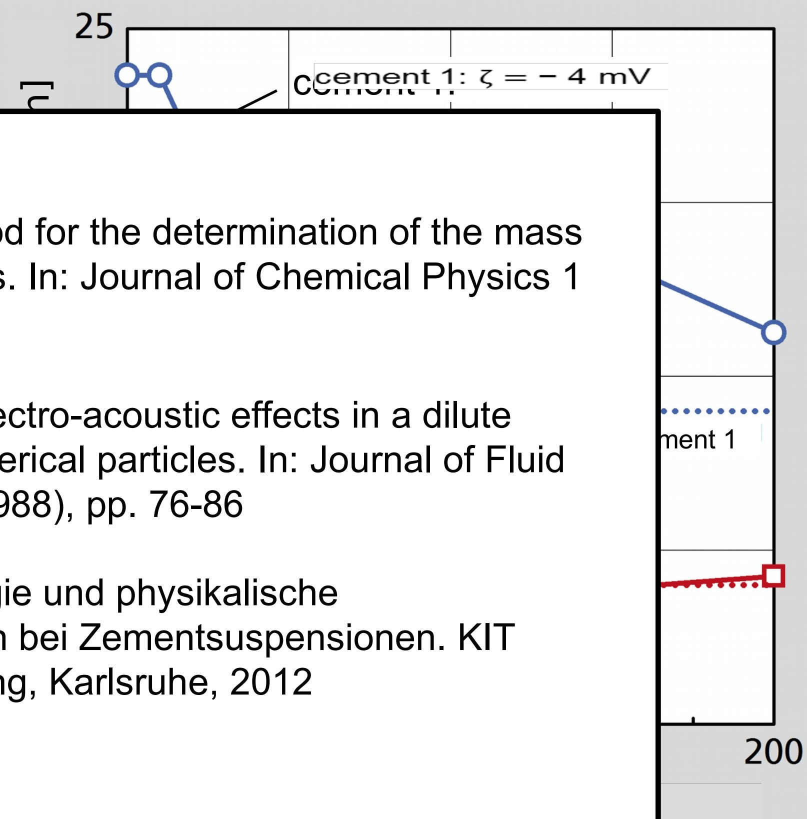
electrica

partic

pressure

ζ-po

Measurement result



Further reading:

Debye, P.: A method for the determination of the mass of electrolytic ions. In: Journal of Chemical Physics 1 (1933), pp. 13-16

O'Brien, R. W.: Electro-acoustic effects in a dilute suspension of spherical particles. In: Journal of Fluid Mechanics 190 (1988), pp. 76-86

Haist, M.: Rheologie und physikalische Wechselwirkungen bei Zementsuspensionen. KIT Scientific Publishing, Karlsruhe, 2012

Rheological modelling

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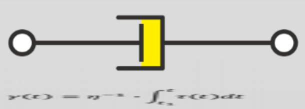
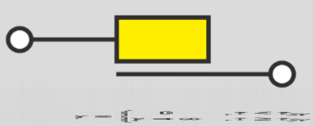
Base elements

spring

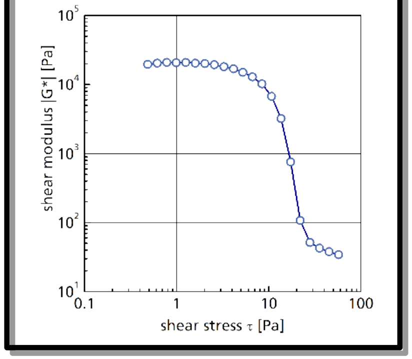
dash-pot



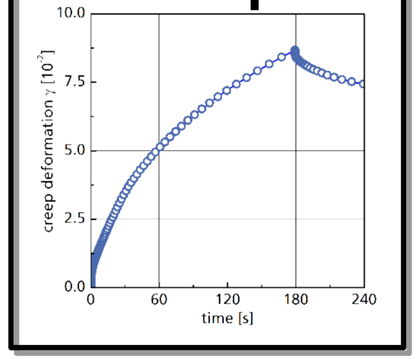
friction element



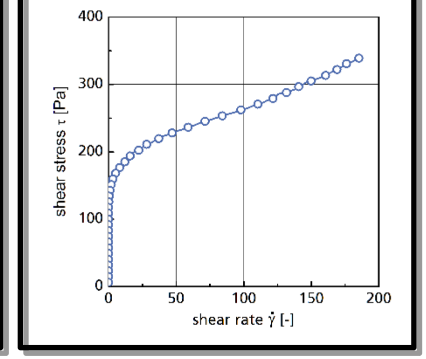
elastic

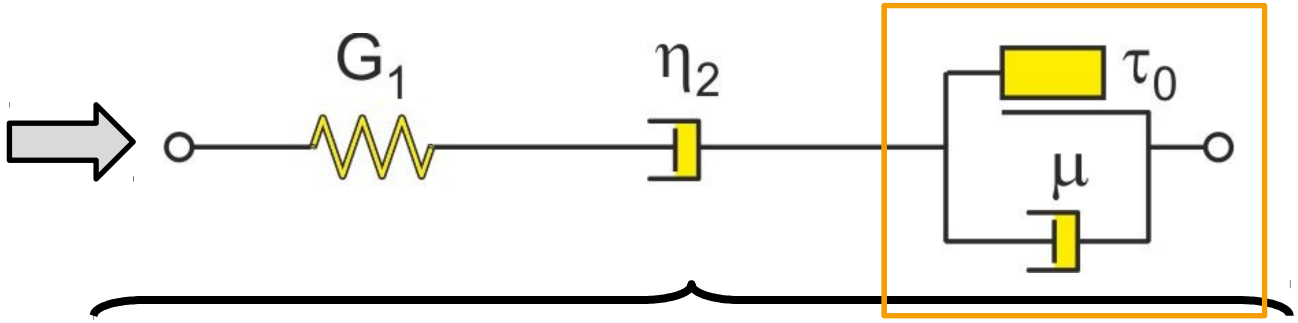


creep



flow





Parameters defined as functions of:

- Blaine value
- mean particle size
- particle mineralogy
- phase content ϕ
- packing density ϕ_p

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Rheology of superplasticizer-modified pastes

State of knowledge

Literature review regarding cement – superplasticizer interaction: qualitative results

	parameter ↑	yield stress τ_0	viscosity μ	SP-adsorption
cement	Blaine-value	↑	↑	↑
	C_3S / C_2S-content	↓	↓	↑
	C_3A / C_4AF-content	↓	→	↑
	alkalinity	↑	↑	↓
	sulfate content	→	→	↓
SP (PCE-based)	charge density	↓	↓	↑
	chain length	↓	↓	→
	molecular weight	→	→	↑
legend:	**increasing** ↑	**decreasing** ↓	**influence not clear** →	

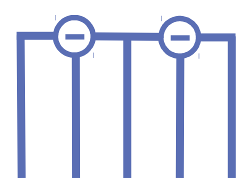
Experimental programme

section	investigation	n	superplasticizer type	superplasticizer name	superplasticizer n	cement	n	sum
0	**reference experiments + determinaton of saturation point**							45
I	**basic cement chemistry**		lignin	L	1	producer A CEM I 32.5 R CEM I 42.5 R CEM I 52.5 R producer B CEM I 42.5 R producer C CEM I 42.5 R producer D CEM I 42.5 R	6	42
			naphtalin	N	1			
			PCE	A / B / C	3			
			PAE	A / B	2			
II	**sulfate agent**	3	PCE	A / B / C / D	4	producer C clinker	1	18
	sulfate content (3.5%)	3	PAE	A / B	2			
III	**SP charge density**		PCE	E / F	2	producer A CEM I 42.5 R producer B CEM I 42.5 R producer C CEM I 42.5 R producer D CEM I 42.5 R	4	12
			PAE	B	1			
IV	**SP chain length**		PCE	D	1			4
							sum (for a single dosage)	121

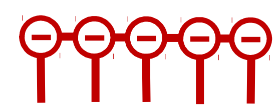
PCE Superplasticizers (examples):

PCE A

PCE B



PCE C



Influence of SP-dosage on yield stress

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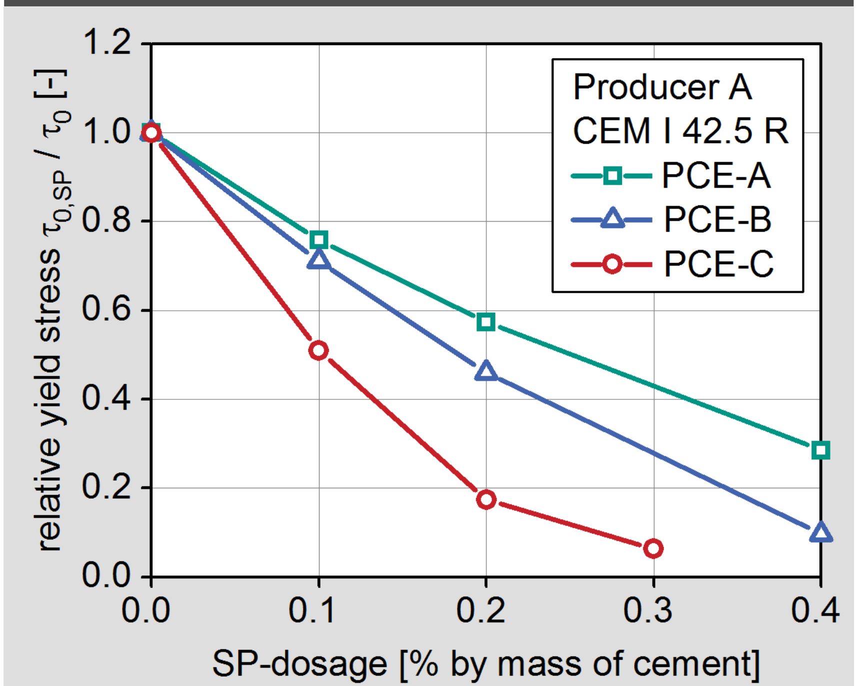
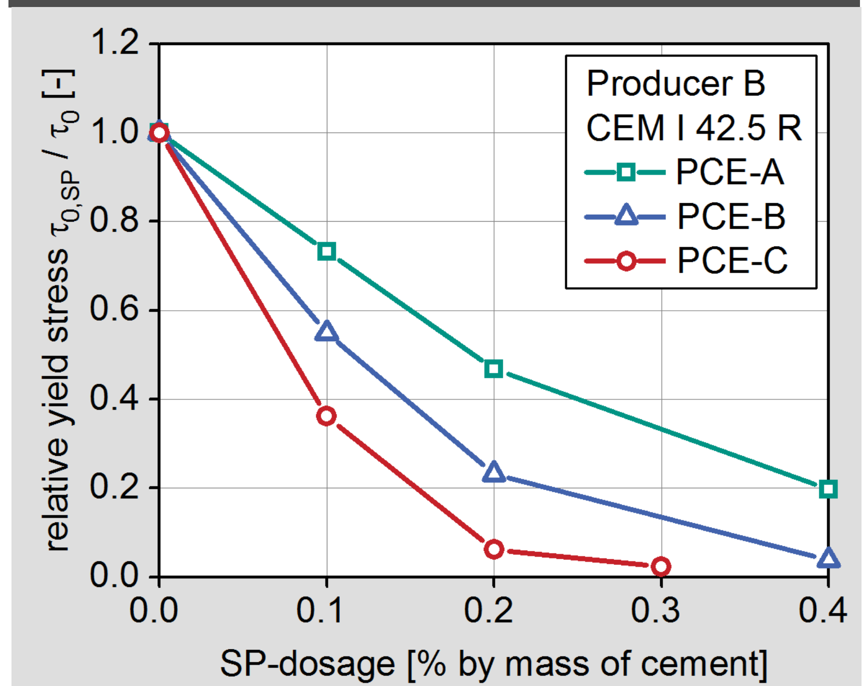
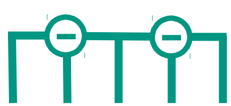
Producer A: CEM I 42.5 R; w/c = 0.4



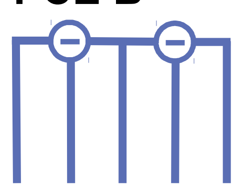
Producer B: CEM I 42.5 R; w/c = 0.4



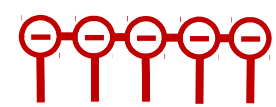
PCE A



PCE B



PCE C



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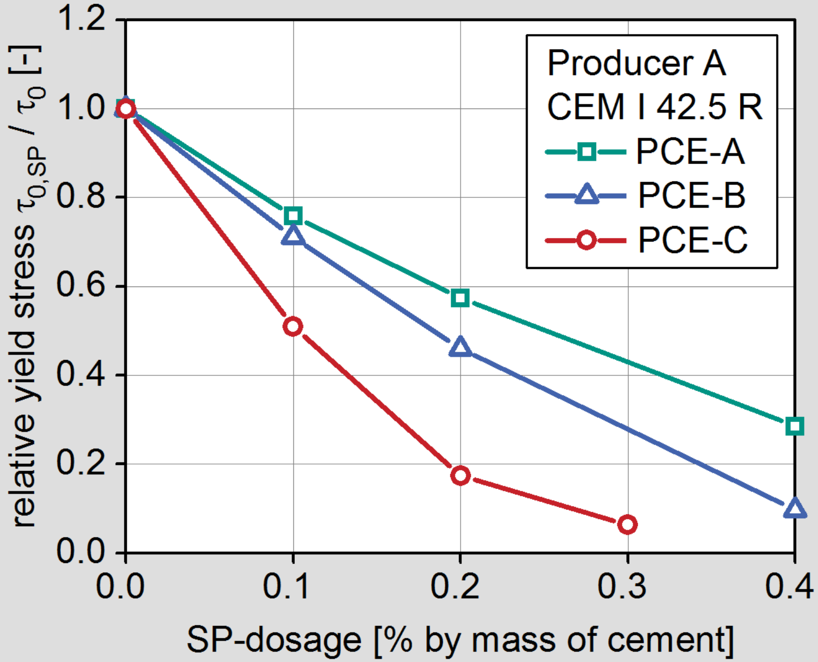
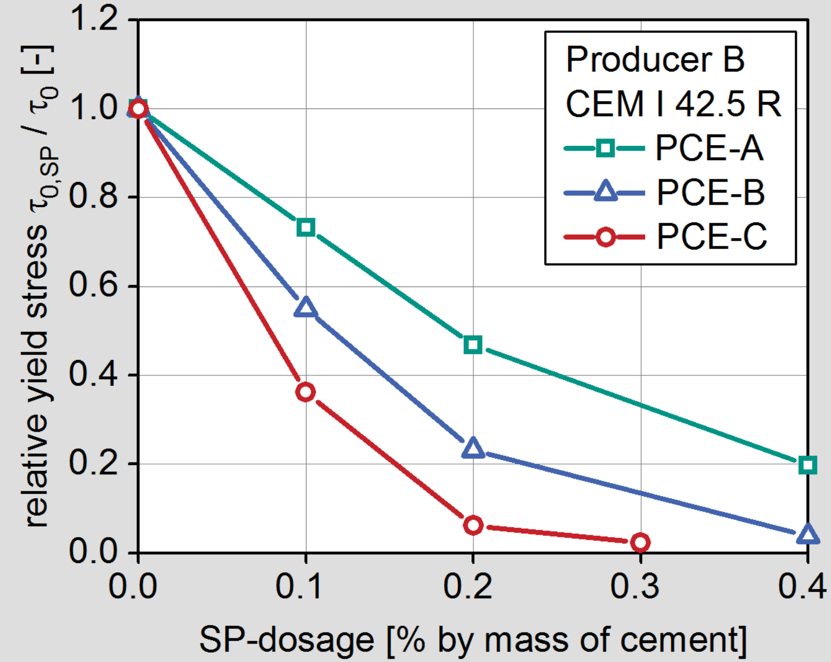


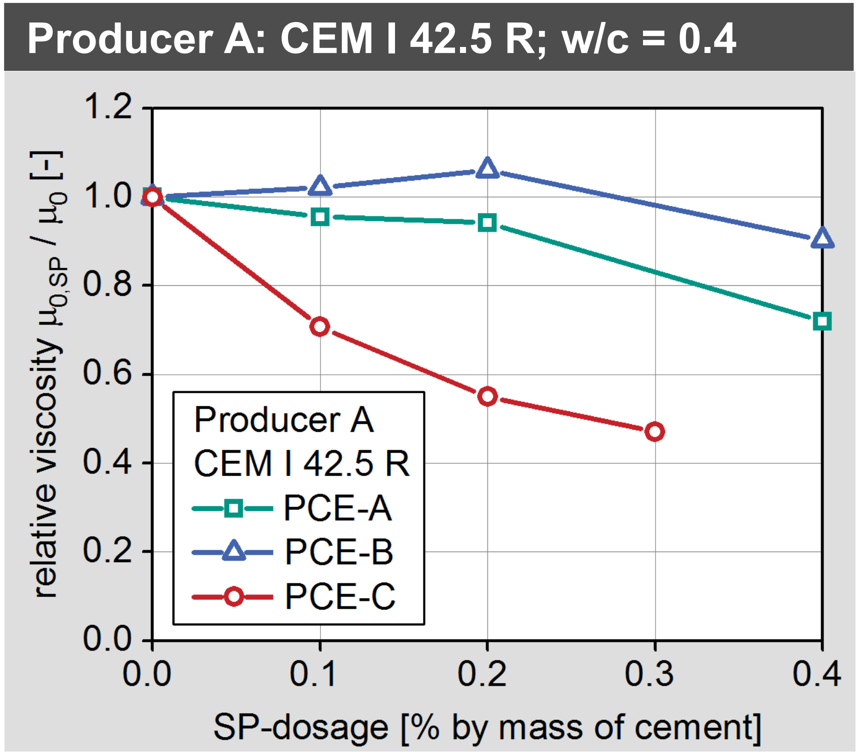
- C_3A-content: 6.4 %
- sulfate content: 3.7 %
- hemihydrate: 1.6 %

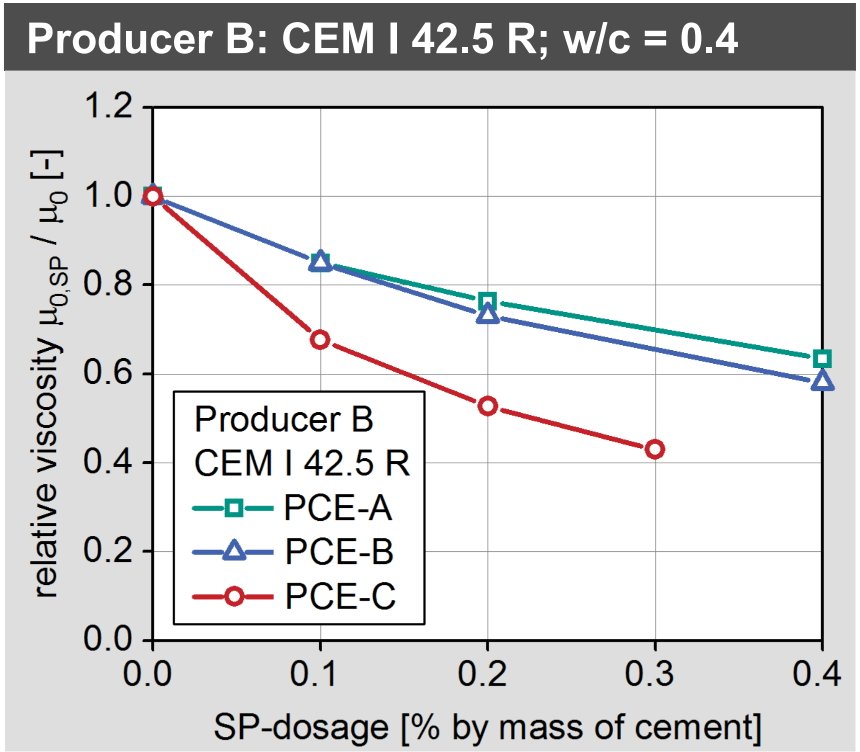
Producer B: CEM I 42.5 R; w/c = 0.4

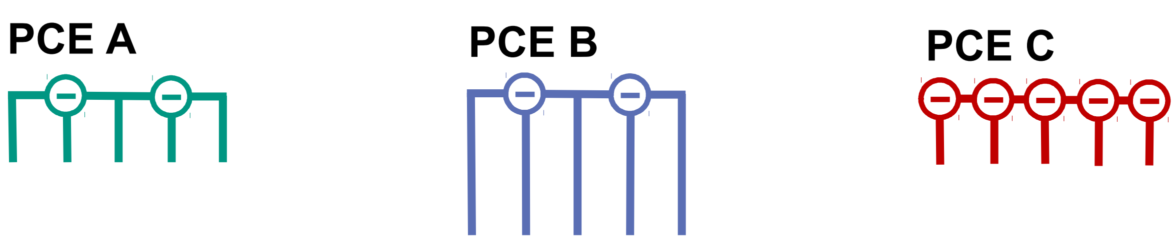


- C_3A-content: 4.9 %
- sulfate content: 4.5 %
- hemihydrate: 1.4 %

Influence of SP-dosage on plastic viscosity







Influence of SP-dosage on plastic viscosity

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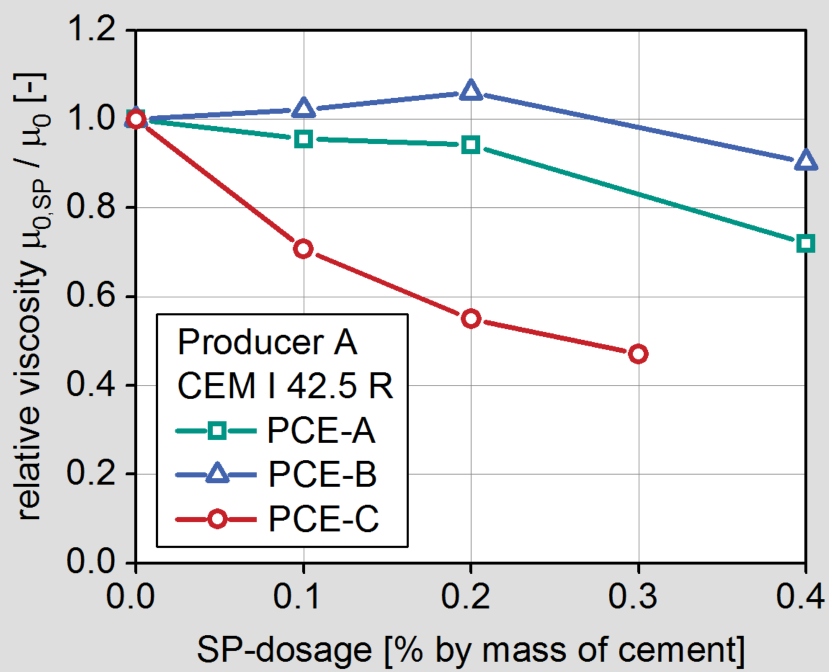
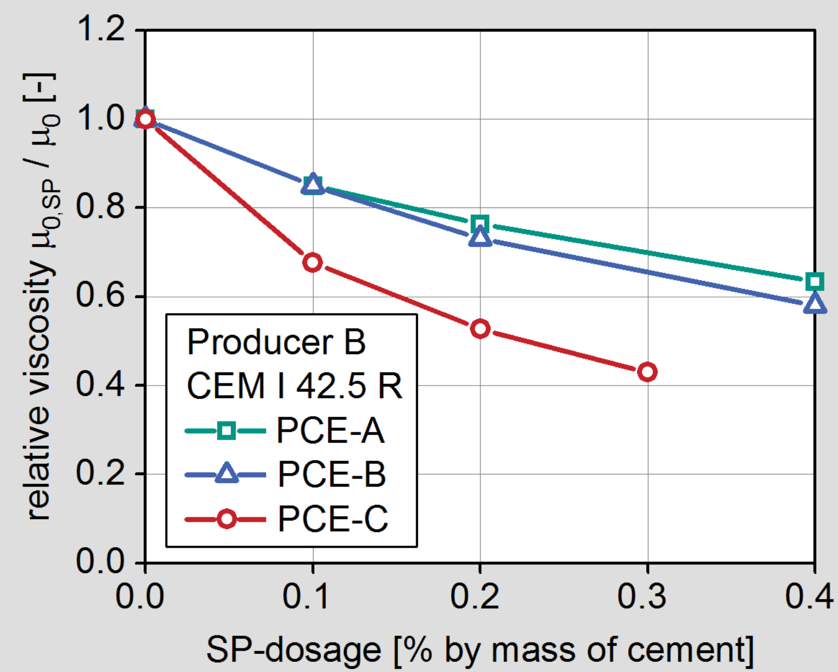


- C_3A-content: 6.4 %
- sulfate content: 3.7 %
- hemihydrate: 1.6 %

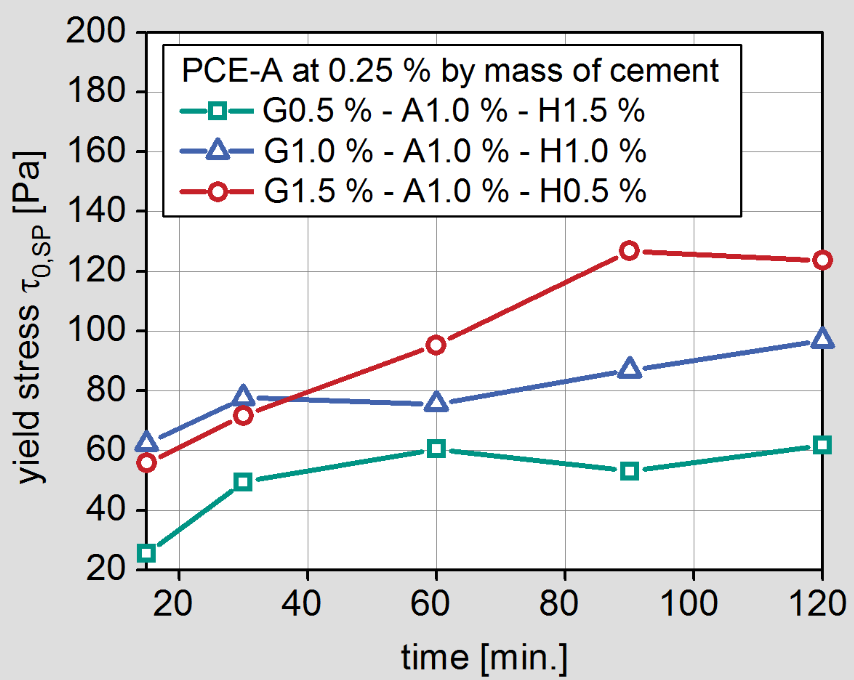
Producer B: CEM I 42.5 R; w/c = 0.4

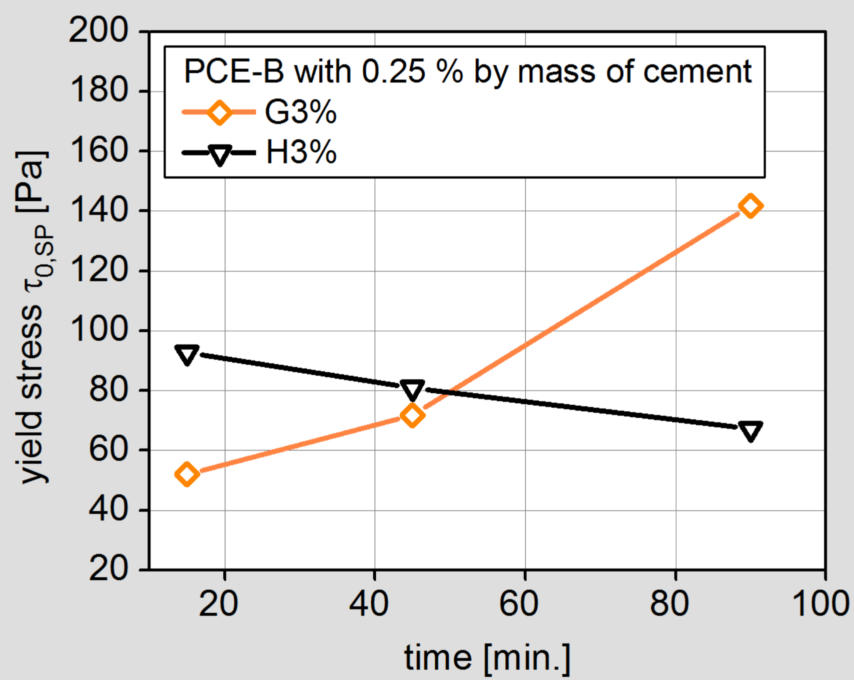


- C_3A-content: 4.9 %
- sulfate content: 4.5 %
- hemihydrate: 1.4 %

Influence of sulfate agent

Producer A: clinker powder CEM I 42.5 R; iron sulfate 0.5 %





Conclusions

- Properties depending on the composition of the sulfate agent
- Increasing part of hemihydrate (H) improves workability

Adsoprtion behaviour of SP

Adsorption of superplasticizer

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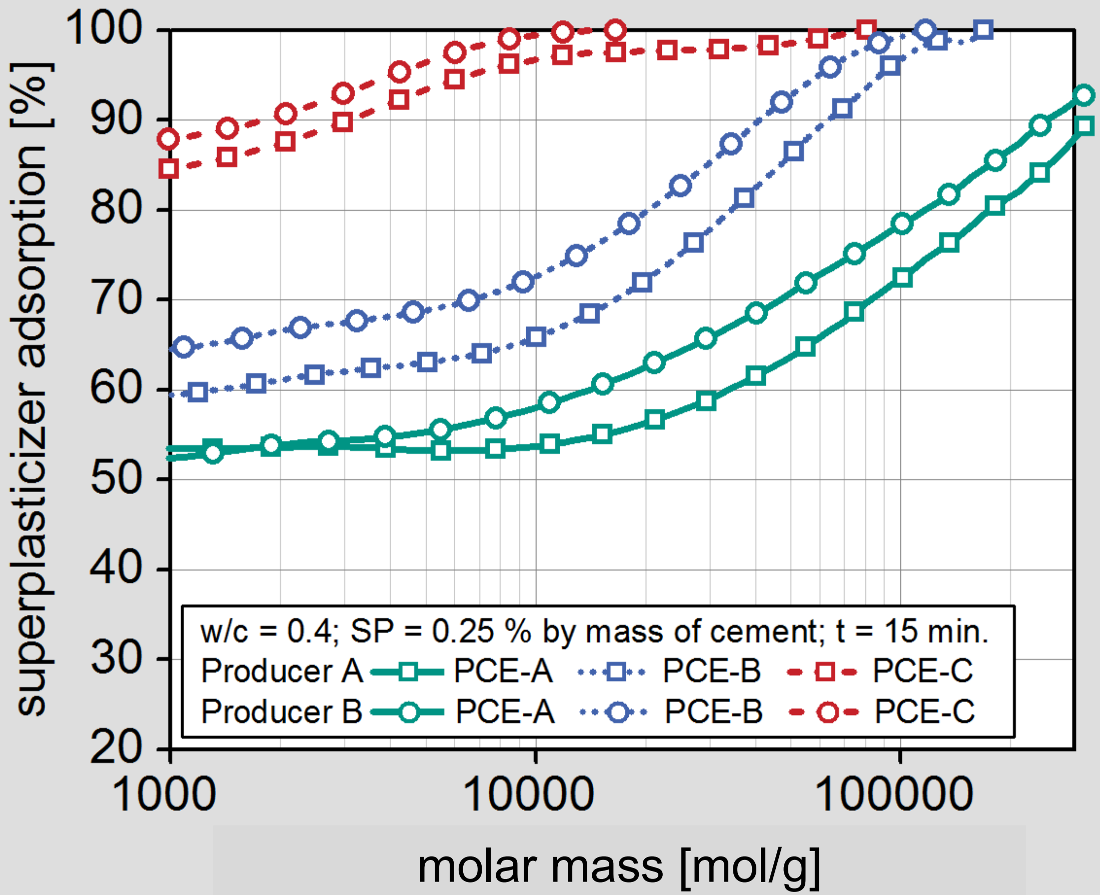
Cement CEM I 42.5 R; w/c = 0.4; extraction of filtrate 15 min after water addition

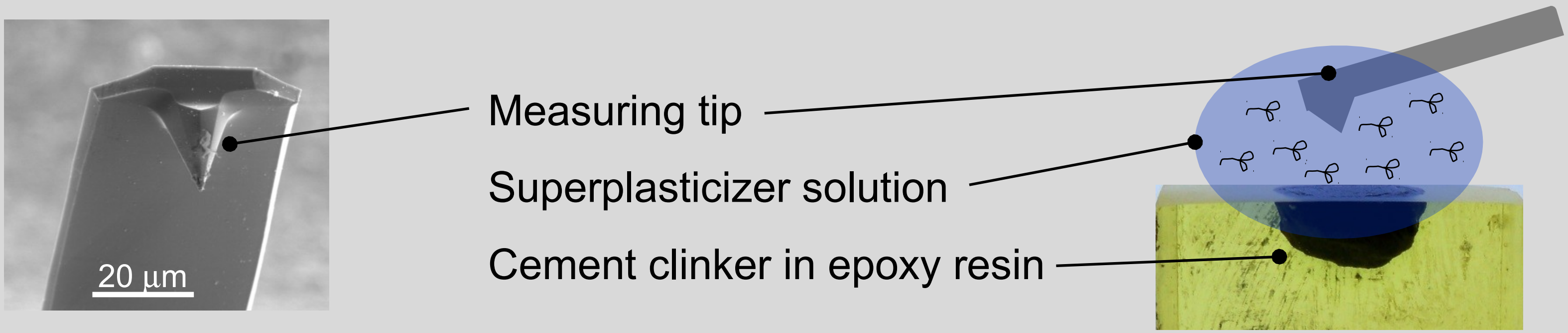
- Size exclusion chromatography (SEC)
- Separation columns with porous gel (defined pore size)

- Small molecules move through the gel
- Bigger molecules through the channels in between



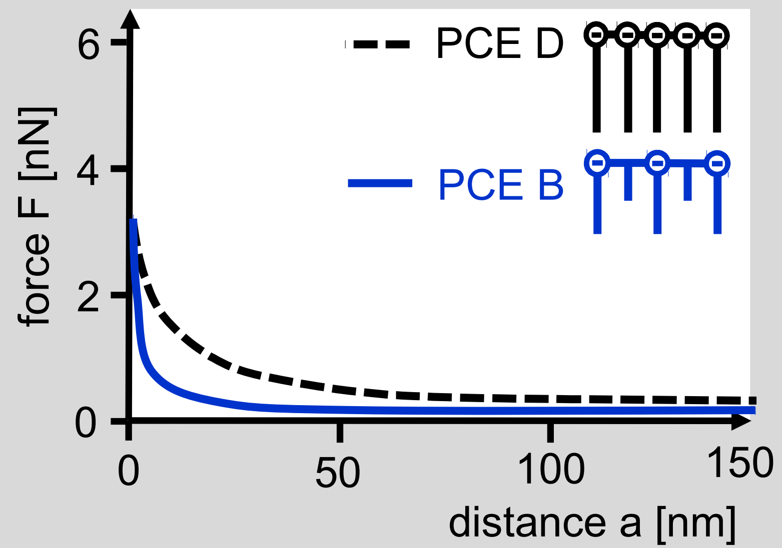
Determination of surface interactions

Atomic-Force-Microscopy (AFM) – Setup and expected results



Results

- Preliminary experiments successful
- Both polymers increase the surface interactions
- as expected PCE D shows higher repulsion forces
- Sample preparation procedure suitable

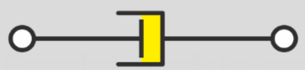


Rheological modelling

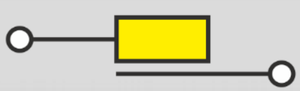
Base elements

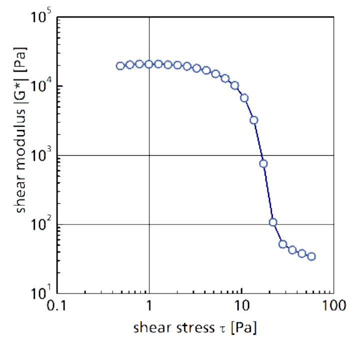
spring

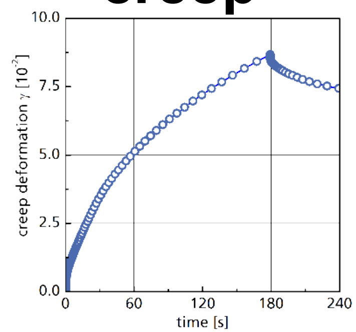
dash-pot

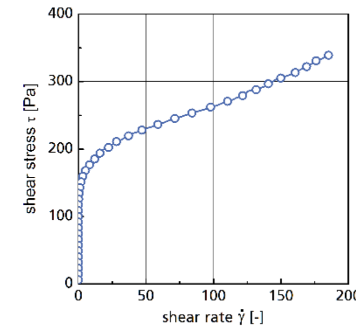


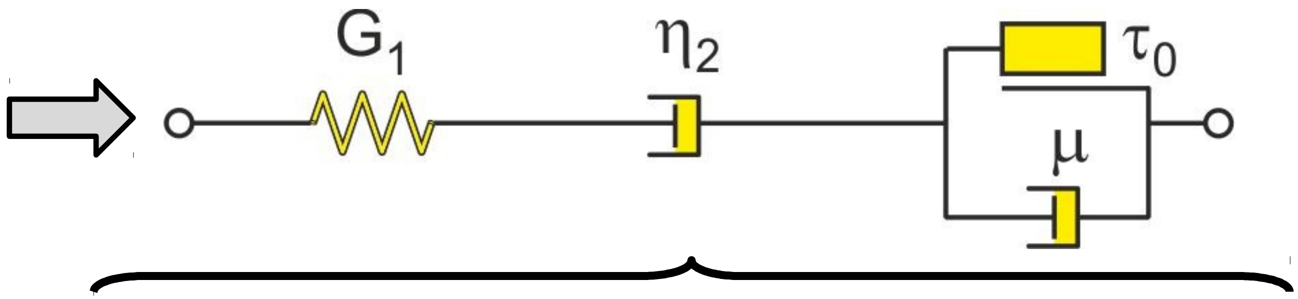
friction element











Parameters defined as functions of:

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- phase content
- packing density

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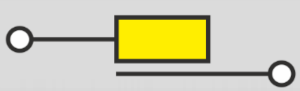
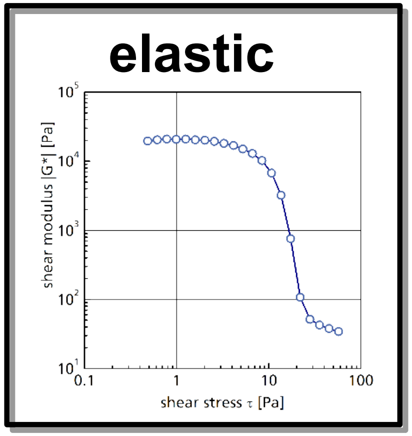
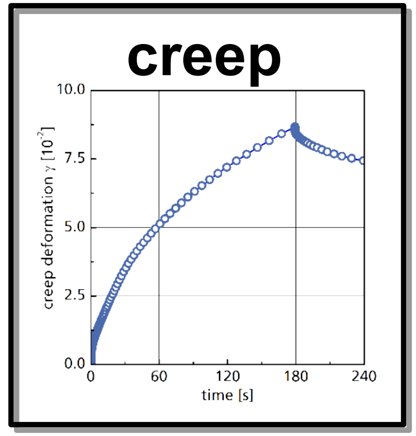
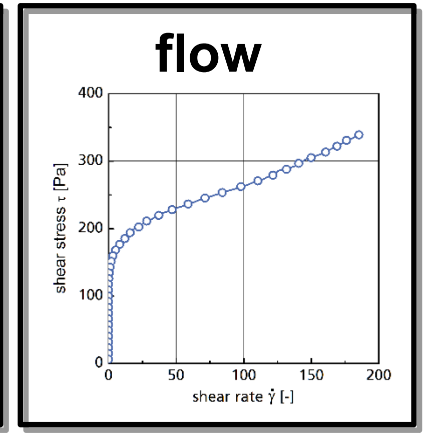
Rheological modelling

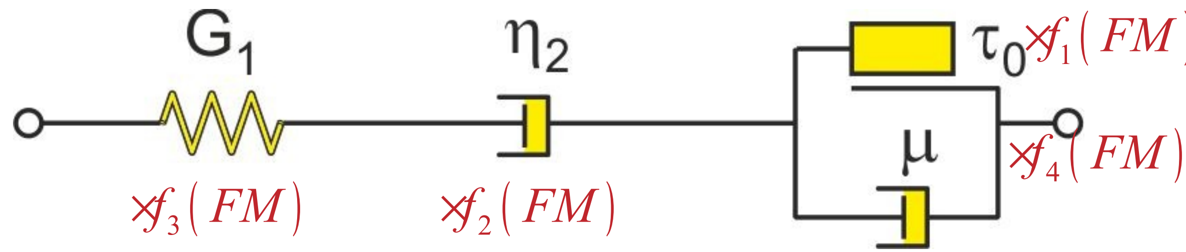
Base elements











Model parameters are modified by SP action

- Consideration of superplasticizer adsorption
- Consideration of sterical interactions

Modelling of superplasticizer interaction

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Example of yield stress calculation for t = 15 min.

$$\tau_0 = 391 \times \exp\left\{ -\left[\frac{3158 \times \Gamma_0}{\Gamma_{C_3S} \times \frac{\phi}{\phi_p}} \right]^2 \right\} \times f\left(c_{C_3A}; c_{C_4AF}; A; c_S; S\right) \times f\left(c_{SP}, m_{ads}, M_W\right)$$

$$\text{with } \Gamma_{C_3S} = \phi \times \rho_p \times c_{C_3S} \times O_{Blaine}$$

- ϕ: phase content
- ρ_p: particle density
- c_{C_3S}: C_3S content
- O_{Blaine}: Blaine value

cement paste model by Haist, 2009

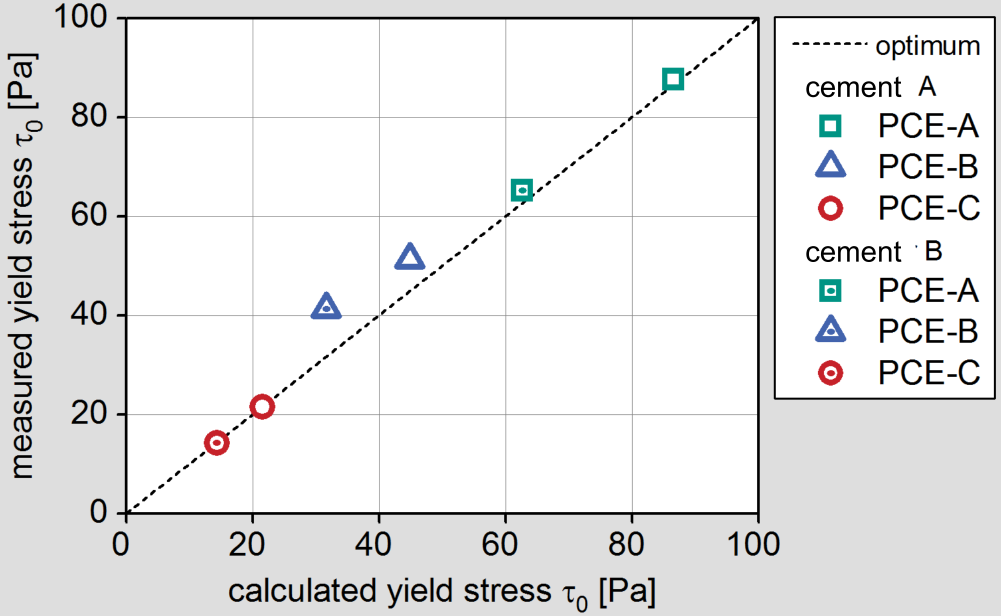
SP adsorption
(C_3A, C_4AF-content, alkalinity, sulfate content, sulfate agent)

Steric hindrance
(SP dosage, mass of adsorbed polymers, molecular weight)

Structure-effect relationship for superplasticizer efficiency

Model validation

Example of yield stress for t = 15 min.



- Input of cement properties

$$\Gamma_{C_3S}; c_{C_3A}; c_{C_4AF}; c_S; S; A$$

- Input of SP properties

$$c_{FM}, m_{ads}, M_W$$

- w/c = 0.4
- t = 15 min.

Conclusions

- Model accounts very well for the underlying interactions
- Careful assessment necessary, as some important parameters still kept constant
- Too limited to be generally accepted at the moment

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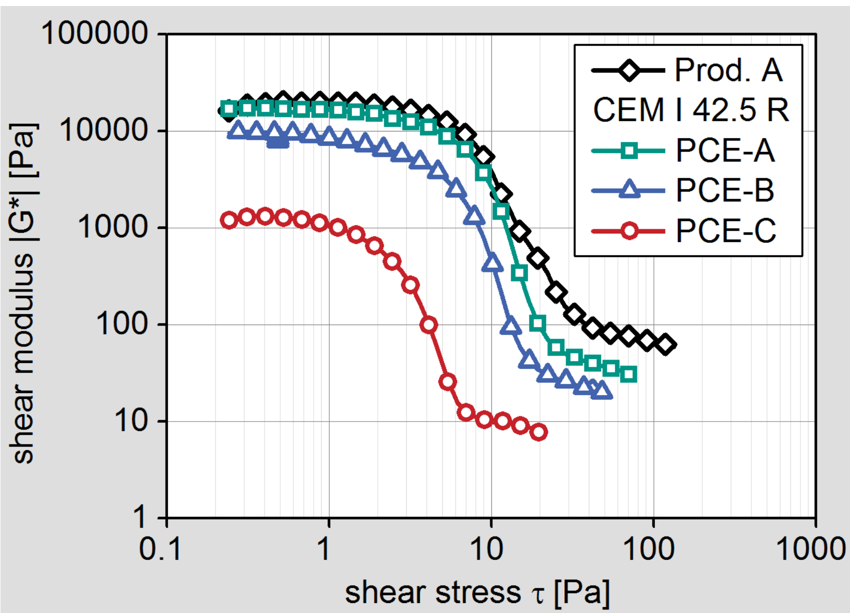
Thank you very much for your attention

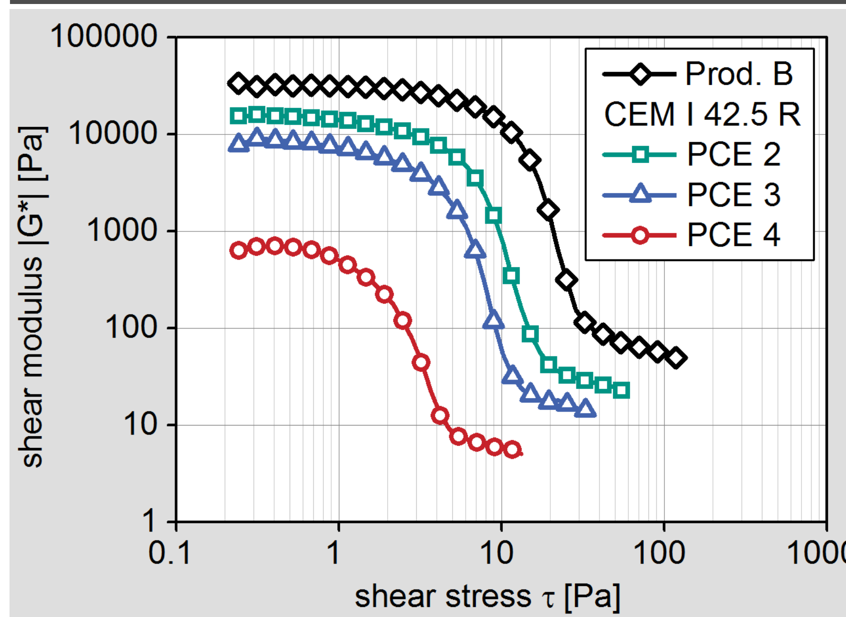
The financing by the Helmholtz Association and the support by OPTERRA and BASF are gratefully acknowledged by the authors.

Behaviour at small shear loadings

Producer A: CEM I 42.5 R; t = 15 min.



Producer B: CEM I 42.5 R; t = 15 min.

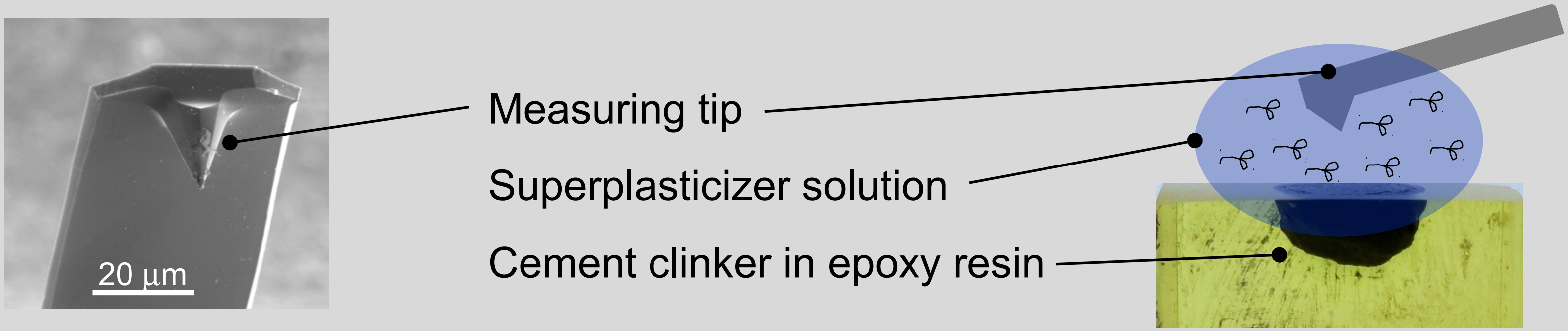


Conclusions

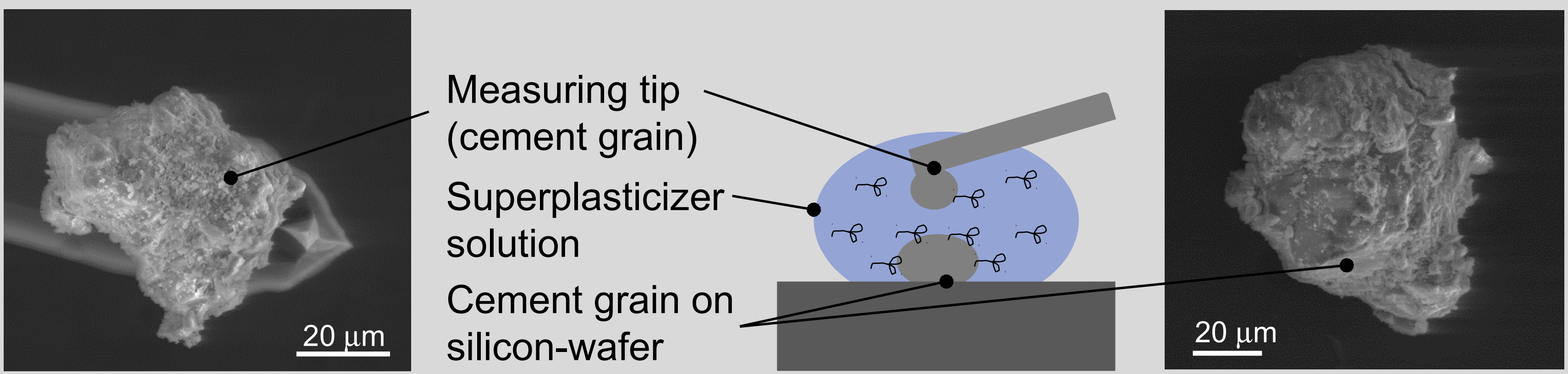
- Rheological behaviour differs clearly
- Elastic properties of the suspension survive despite a SP-addition

Current investigations AFM

So far: Measurement SiO_2 – cement clinker



Now: Measurement cement grain on cement grain



Structure-effect relationship for superplasticizer efficiency

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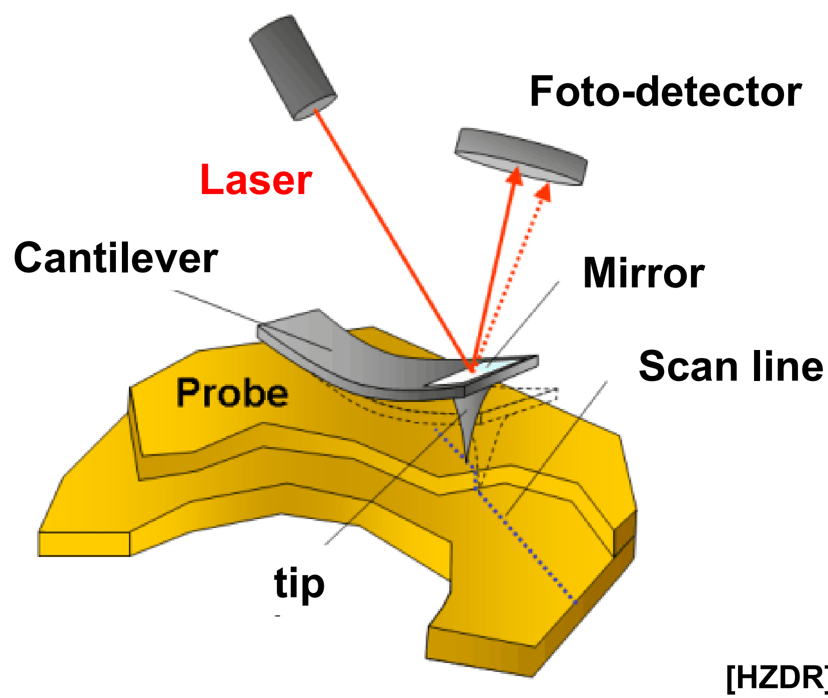
Determination of surface interactions (1)

Atomic-Force-Microscopy (AFM) – principle

- „Raster-Kraft-Mikroskopie“

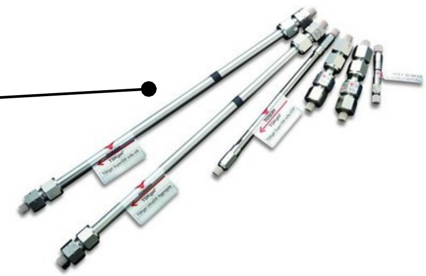
- Bending of a tip (cantilever) depending on the position as a measure for surface forces
- Force-distance-curves to describe the superplasticizer interactions

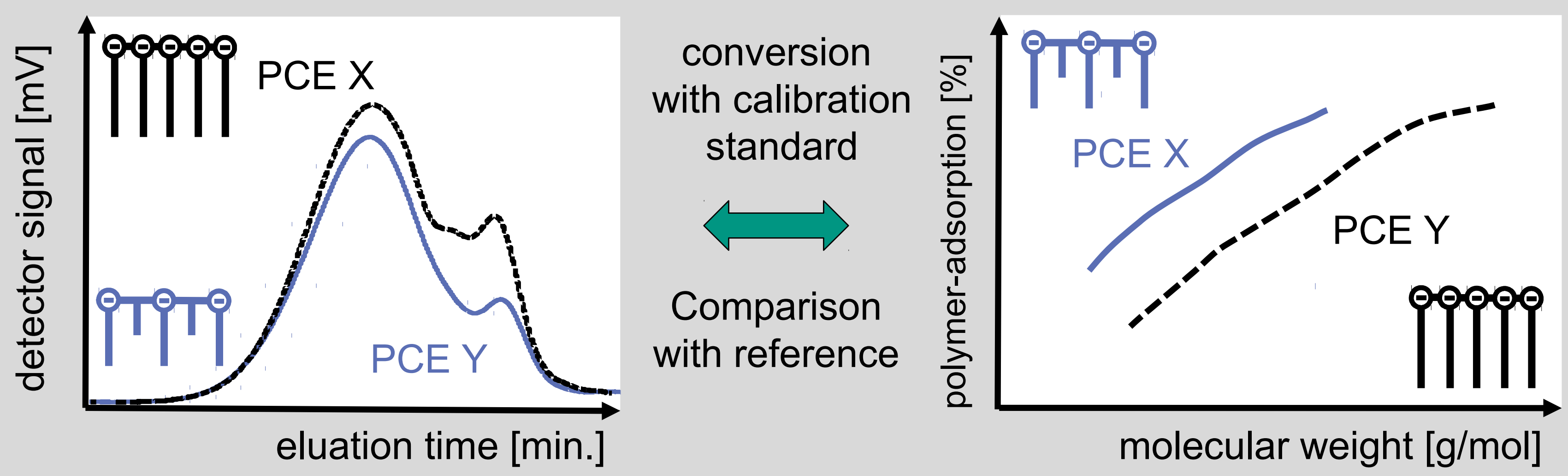


Determination of adsorption behaviour

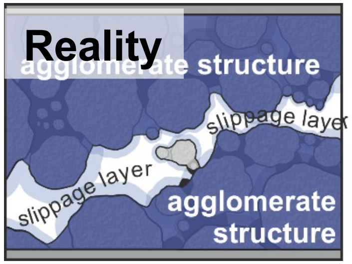
Size exclusion chromatography (SEC)

- „Gel-Permeations-Chromatographie“ (GPC)
- Separation column with porous gel (defined pore size)
- Small molecules move through the gel
- Bigger molecules through the channels in between

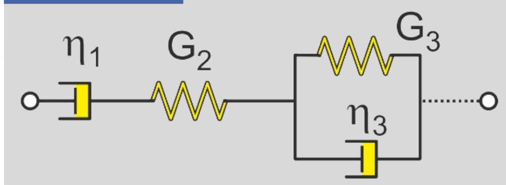




Modelling for pure cement pastes



Model



model characteristics:

- shear modulus G
- viscosity ...

Limitation of current model

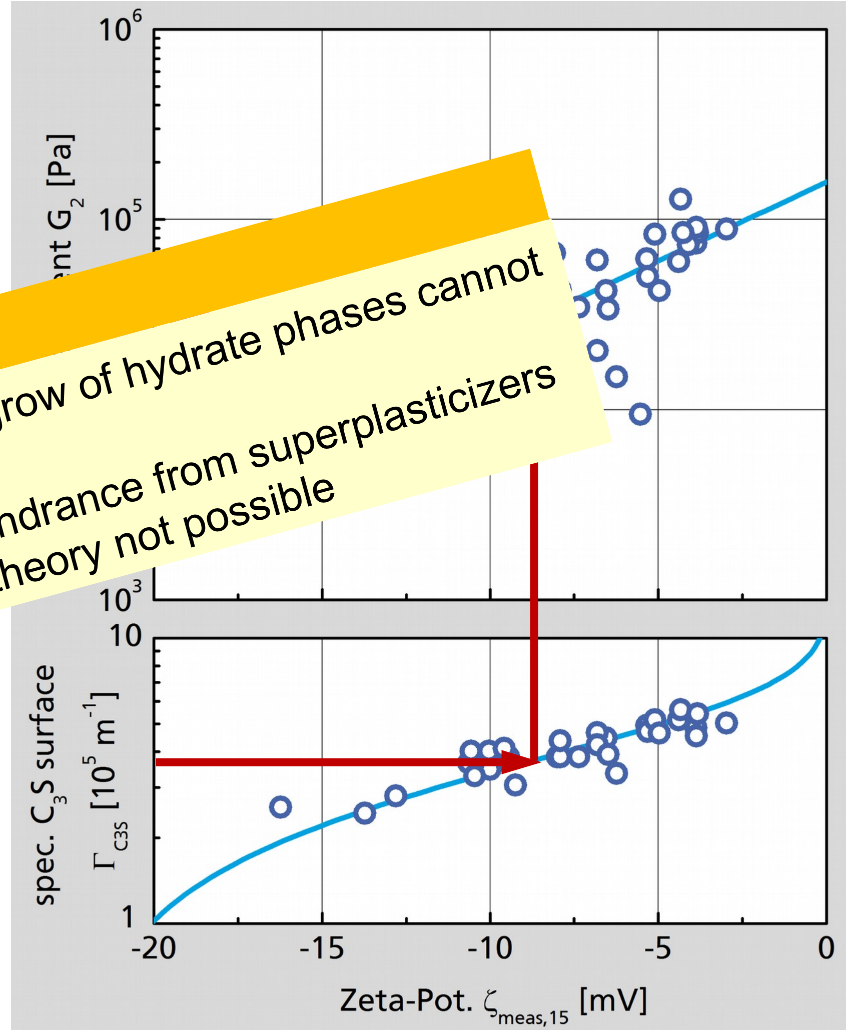
- Interaction effects from the grow of hydrate phases cannot be considered
- Consideration of sterical hindrance from superplasticizers by limitation to the DLVO-theory not possible

prediction of mo... based on Zeta p... ζ

⇩

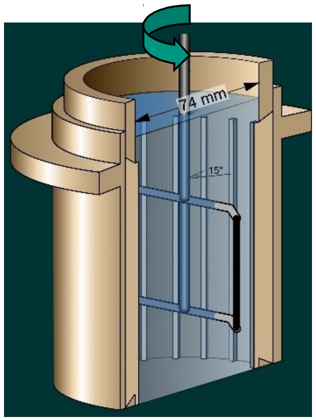
prediction of Zeta potential based on raw material characteristics

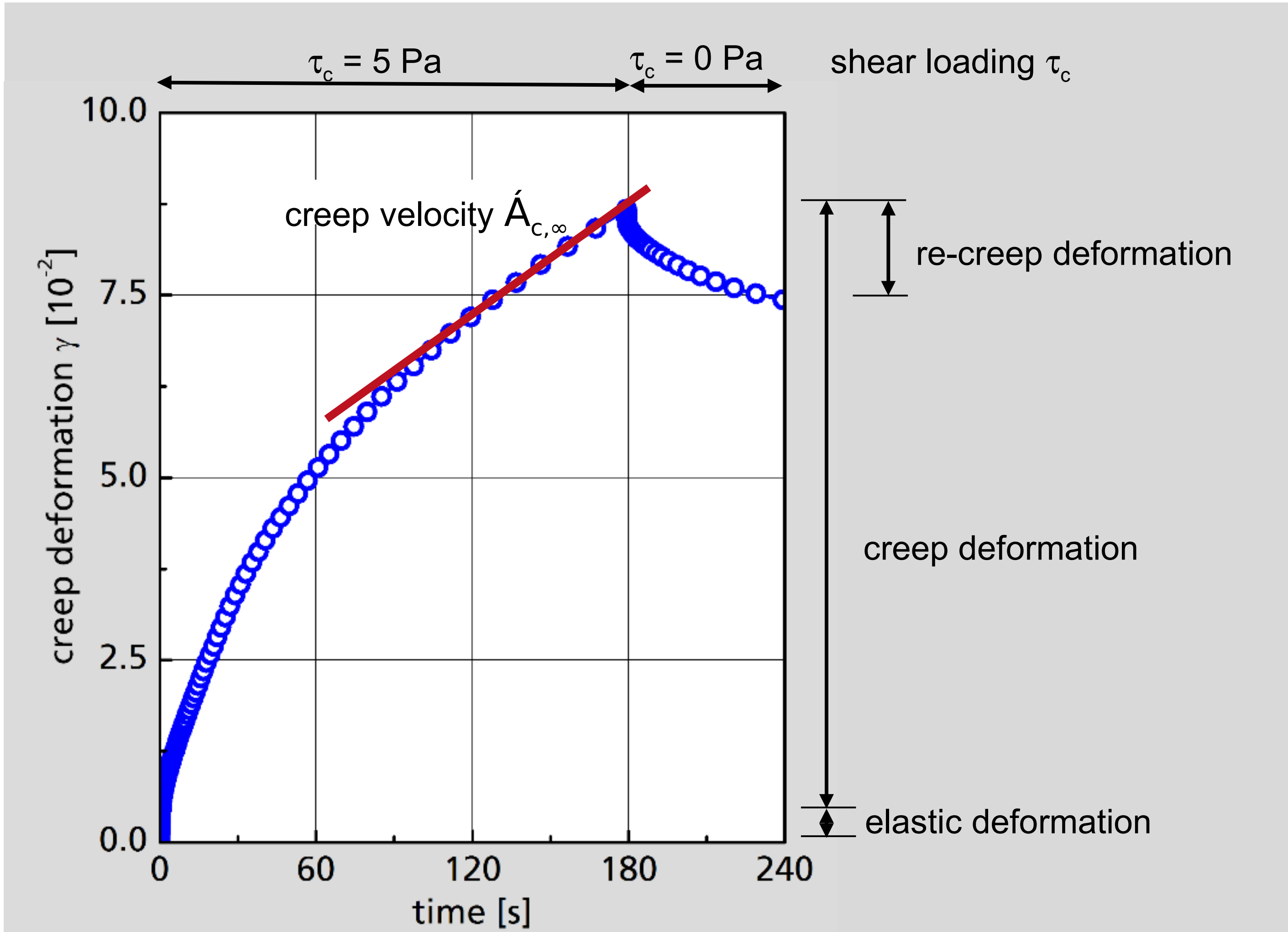
- fineness
- density
- mineralogy
- others



Creep deformation at subcritical shear stresses

Karlsruhe Institute of Technology





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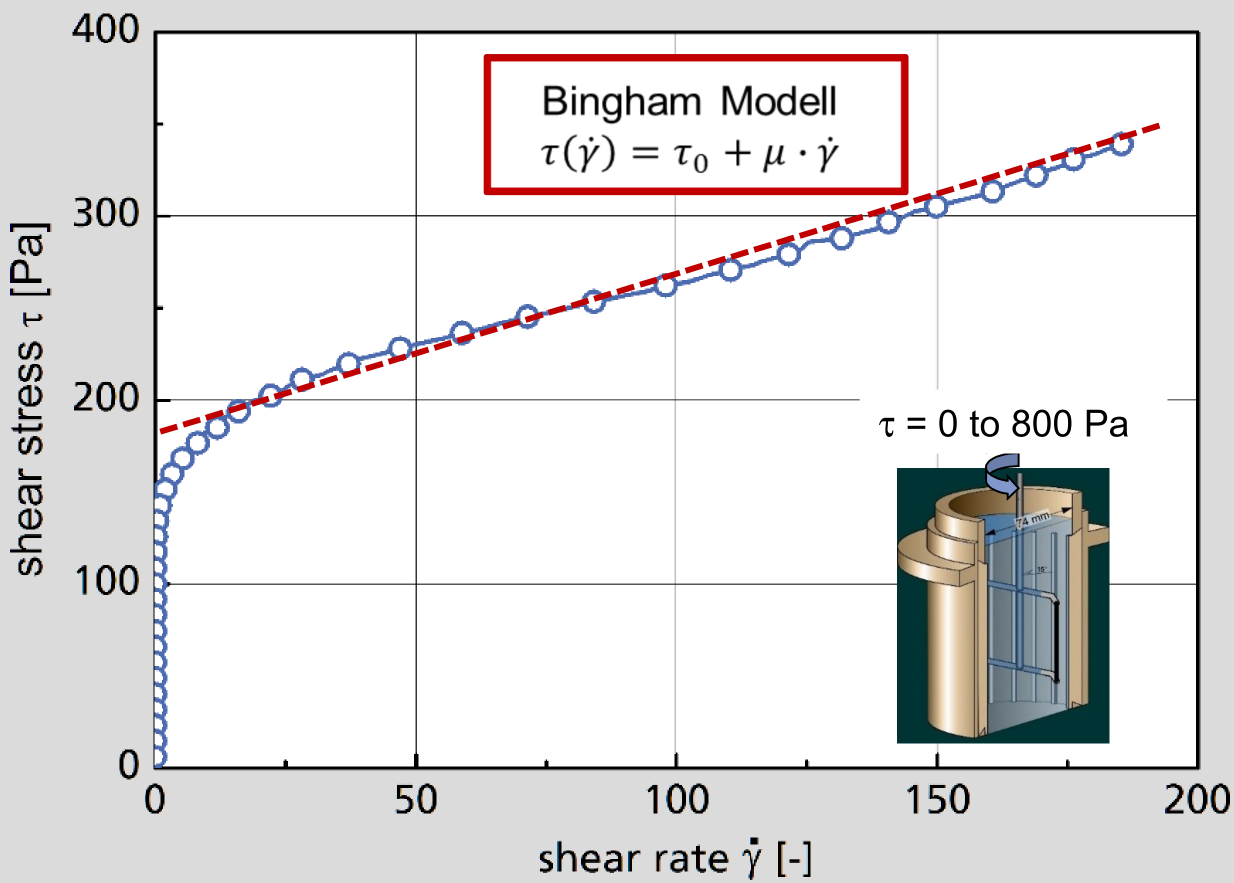
Department Building Materials

Flow behaviour of fresh cement pastes

Karlsruhe Institute of Technology

Flow behaviour



Conclusions

- viscous behavior at low shear rates
- pronounced loss in dynamic viscosity for increasing shear rate

Modelling of superplasticizer interaction

Example of yield stress calculation for t = 15 min.

$$\tau_0 = 391 \times \exp\left\{ -\left[\frac{3158 \times \Gamma_0}{\Gamma_{C_3S} \times \frac{\phi}{\phi_p}} \right] \right\}^2 \times f\left(c_{C_3A}; c_{C_4AF}; A; c_S; S\right) \times f\left(c_{SP}, m_{ads}, M_W\right)$$

$$with \quad \Gamma_{C_3S} = \phi \times \rho_p \times c_{C_3S} \times O_{Blaine}$$

ϕ phase content

- Consideration of superplasticizer adsorption
  (C_3A-content c_{C_3A}, C_4AF-content c_{C_4AF}, alkalinity, sulfate content c_S, sulfate agent)
- Consideration of sterical interactions
  (SP dosage, mass of adsorbed polymers, molecular weight)

➡ **Structure-effect relationship for superplasticizer efficiency**